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Lubrication

A Technical Publication Devoted to the Selection and Use of Lubricants

THIS ISSUE

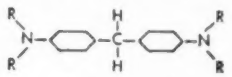
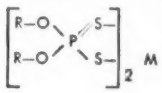
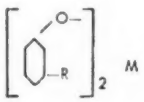
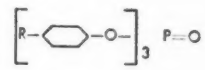
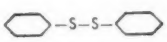
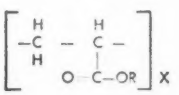
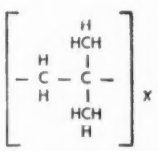
Lubricating Oil Additives

PUBLISHED BY
THE TEXAS COMPANY
TEXACO PETROLEUM PRODUCTS

Improved Lubrication

DUE TO USE OF ADDITIVES

A Lubricating Oil Additive is a Chemical Compound Which Is Added to a Lubricant to Improve Its Qualities and Performance.

TYPE OF ADDITIVE	TYPICAL FORMULA	FUNCTION IN LUBRICANT
Anti-Oxidant Organic Amine		Increase the Resistance of Oil to Oxidation
Anti-Corrosive Metal Salt of a Thiophosphoric Acid		Decrease or Prevent Bearing Corrosion
Detergent Metallic Sulfonate		Promote General Engine Cleanliness
or Metallic Phenolate		
Extreme Pressure Agent Phosphorus–Containing Organic Compound		Impart High Load Carrying Properties to a Lubricant
or Sulfur – Containing Organic Compound		
Pour Depressant High Molecular Weight Polymer		Reduce the Pour Point of an Oil So That It Will Flow Freely at Reduced Temperatures
or Wax Naphthalene Condensation Product		
Viscosity Index Improver High Molecular Weight Resin		Improve the Viscosity-Temperature Relationship of Lubricants

NOTE: In the above formulas, the following symbols are used:

(1) M = a metal
(2) R = an organic group composed of hydrogen and carbon
(3) X = indicates a number of like molecules condensed together to form a resin-like material
(4) Wax = high molecular weight paraffinic hydrocarbon

LUBRICATION

A TECHNICAL PUBLICATION DEVOTED TO THE SELECTION AND USE OF LUBRICANTS

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Lubricating Oil Additives

THE STORY of additives in lubricants is not new, but their use in lubricating oils to any great extent was not a major consideration in this country until the last decade. It was during that period that the Diesel engine, which had formerly been used only as a large, low-speed prime mover for power plant and marine service, increased in popularity when the smaller sized medium and high-speed engine was developed for use in tractors, trucks, buses and industrial applications.*

Along with the many changes and improvements in mechanical design brought about by these new engines, came lubrication difficulties which had to be overcome by the oil refiner with the cooperation of the engine manufacturer. These difficulties, such as ring sticking and piston scuffing, were remedied by the use of additives in the lubricating oil. The name given to this first type of Diesel oil additive was "detergent". Typical of this improvement was the additive oil developed for use in the Caterpillar Diesel engine about ten years ago.

Heavy Duty Motor Oils

Improvements in lubricants did not stop with the development of "detergent" oils, however. Further changes in engine design created additional problems, such as oil oxidation and bearing corrosion, which had to be overcome by the lubricating oil technologist. During the years directly preceding and including World War II, great strides were made in developing oils which would perform satisfactorily under the severe conditions encountered in these new and improved engines.

Gradually the "heavy duty" motor and Diesel oil came into being. In addition to the "detergents" used in the Diesel oils of ten years ago, heavy duty motor oils contain other additives, such as anti-oxidants and anti-corrosives, designed to greatly improve the performance qualities of the base oil. Heavy duty oils are recommended today for use in all high-speed, heavy load equipment, such as buses, trucks, and tractors equipped with diesel or gasoline engines.

What Are Additives?

Before proceeding further, it is well to find out what is meant by the word "additive". A lubricating oil additive may be defined as a chemical compound* which either imparts new properties to an oil or else improves those properties which the oil already has. As a rule, rather low concentrations of additives, in the range of 0.01 to 5.0 per cent, are sufficient to achieve the desired results.

All lubricating oil additives may be divided into two major classes:

(1) Those which are useful for their properties as associated with the phenomenon of oil oxidation, such as anti-oxidants, anti-corrosives, and detergents.

(2) Those which are added to an oil to improve some physical property of the oil, such as viscosity index, pour point, film strength, rust-protection, and foaming characteristics.

Additives Are Here To Stay

As mentioned above, heavy duty motor oils must provide good lubrication under extremely severe conditions. Oils of this type containing carefully

*LUBRICATION, November, 1943.

*Definition of "additive" – while unquestionably the ingredients are chemical compounds, many commercial additives are mixtures, and sometimes the exact chemical structure of the active ingredients is uncertain.

selected additives have proved in service the prediction of the research laboratories as to their protective ability under heavy duty engine service.

Since additives have done such a remarkable job in improving both the chemical and physical properties of heavy duty motor oils, there is a definite trend at the present time to incorporate similar materials in oils used for lubricating other types of equipment including aircraft engines, automobiles, railway Diesels, and turbines. If the type and number of engine developments which have occurred during the past ten years is any indication of what will happen in the future, it is safe to assume that the importance of lubricating oil additives will continue to grow.

Oil Oxidation

Various factors enter into the failure of a lubricant to do its job, but the major cause of oil deterioration is oxidation. Any lubricating oil which is exposed to oxygen (or air) at any temperature will eventually oxidize. The length of time before this takes place and the extent to which it occurs depends on a number of factors including temperature,

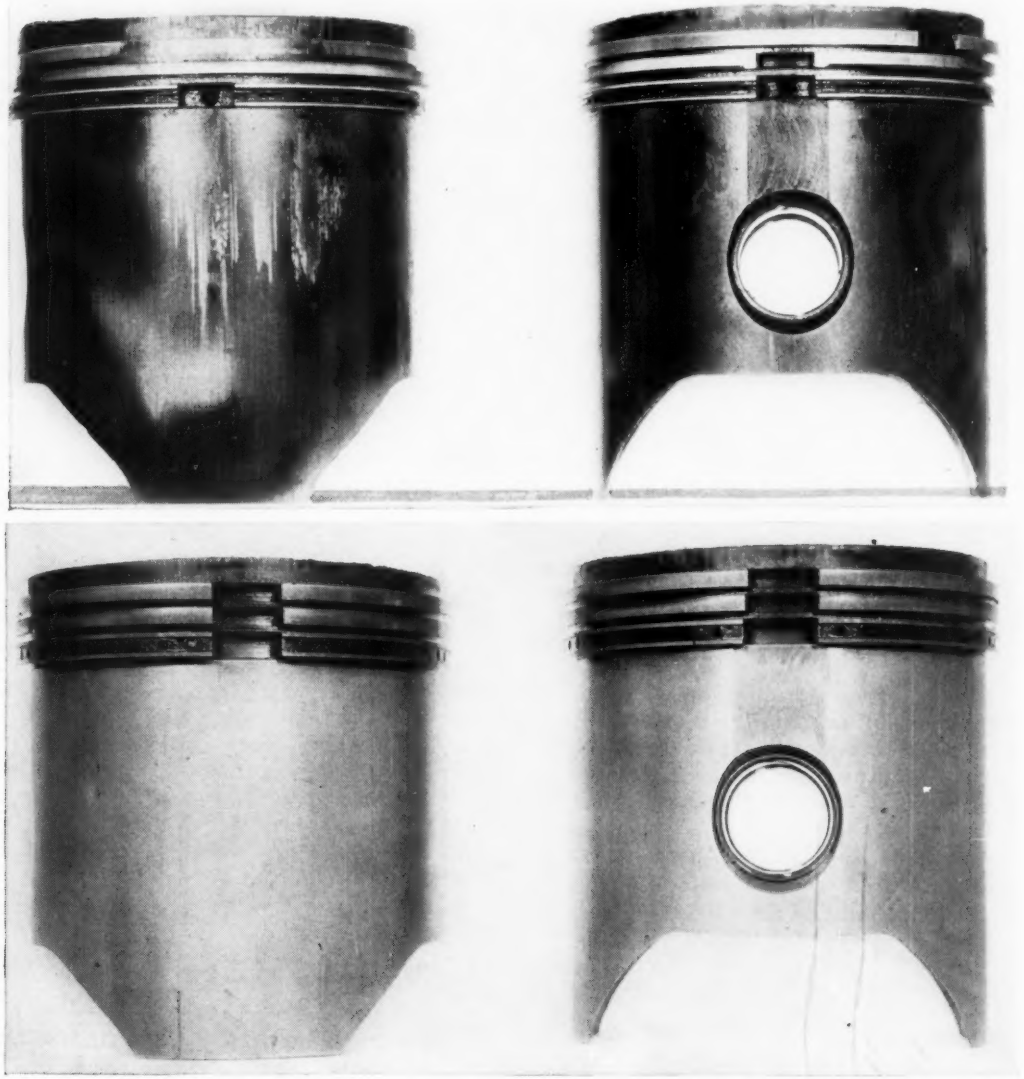

Figure 1—Showing pistons from a Chevrolet Deposits Test. Above are front and side views of a piston from a test run on a straight mineral SAE 20 Motor Oil. Below are front and side views of a piston from a test run on the same oil plus an anti-oxidant.

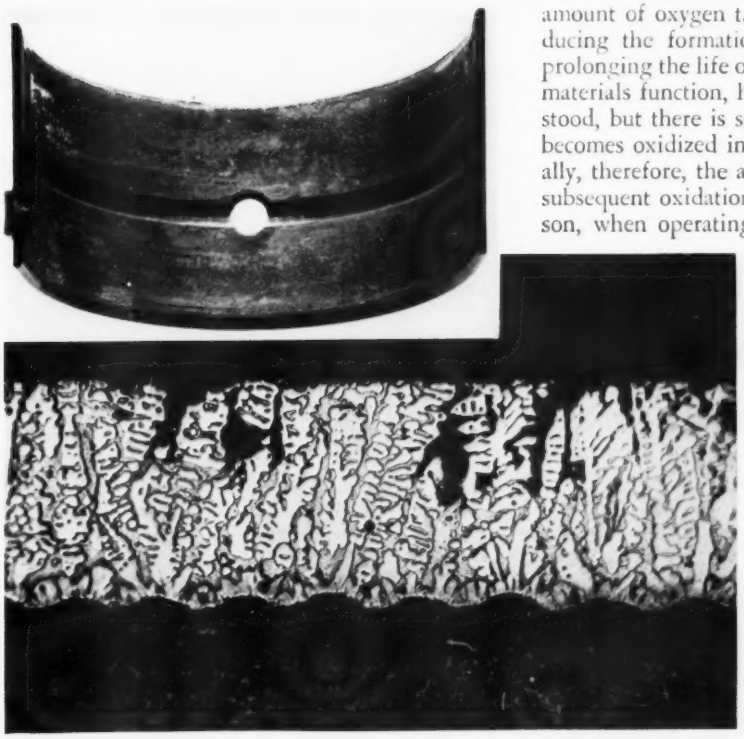

Figure 2—Showing a corroded bearing due to use of an uninhibited oil. "A" shows the appearance of the bearing shell. "B" shows a photomicrograph of its bearing structure indicating how the lead has been eaten away.

amount of oxygen and catalytic metals present, and the ability of the oil to withstand oxidation. The products of oxidation are numerous. Many of these are acidic which ultimately lead to bearing corrosion.

Prolonged oxidation of the oil results in the formation of sludge which is so often the cause of clogged oil lines, filters, and screens. The oxidized materials may, under high temperature conditions, link together, or polymerize, to form varnish and lacquer on pistons, cylinders, and other engine parts. All of these oxidized products tend to lower the efficiency of the engine and quite often lead to engine failure. As implied above, oxidation is promoted by the catalytic effect of certain metals. Iron and copper are probably the worst offenders of this type encountered.

ANTI-OXIDANTS

Additives which increase the resistance of an oil to oxidation are called anti-oxidants. In general, anti-oxidants are organic compounds containing sulfur, phosphorus, or nitrogen, such as organic amines, sulfides, hydroxy sulfides, and phenols. Metals, such as tin, zinc, or barium, are also often incorporated in the additives to improve their properties. The anti-oxidant greatly decreases the amount of oxygen taken up by the oil, thereby reducing the formation of acidic bodies, etc., and prolonging the life of the oil. Just exactly how these materials function, however, is not too well understood, but there is some evidence that the additive becomes oxidized in preference to the oil. Eventually, therefore, the additive becomes depleted with subsequent oxidation of the oil itself. For this reason, when operating any equipment under conditions such that oxidation can take place, periodic oil changes should be made even though the new oil may contain an excellent anti-oxidant.

Since engine evaluation of lubricants is costly and time-consuming, a number of bench tests have been developed to determine the relative merits of anti-oxidants. Data illustrating anti-oxidant action in one such bench test are given below. The test procedure consists of oxidizing a sample of oil for forty hours at 338° F. The amount of oxygen absorbed by the oil during that time is recorded. In addition, the oxidized oil is subjected to various chemical and physical tests, such as viscosity, neutralization number and amount of dissolved and undissolved sludge, in order to determine the degree and type of oxidation which has taken place.

Additive	*Units Oxygen Absorbed*
None	300
1% of a Phenol	219
1% of a Phosphite	105
1% of an Amine	89

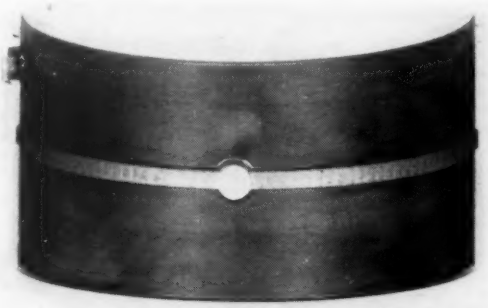

Figure 3—Shows a bearing shell surface indicating the benefits of using an anti-corrosive additive.

Data such as these show the relative ease of oxidation of the base oil and the inhibited oils and indicate to the petroleum chemist which type of additive will most effectively prolong the life of the oil.

Bench tests of the type mentioned are very helpful in giving an indication of the anti-oxidant properties of additives. It should be emphasized, however, that they do not eliminate the necessity for full-scale engine tests since there are numerous factors in engine operation affecting the oxidation of oils which cannot be satisfactorily reproduced in any bench test.

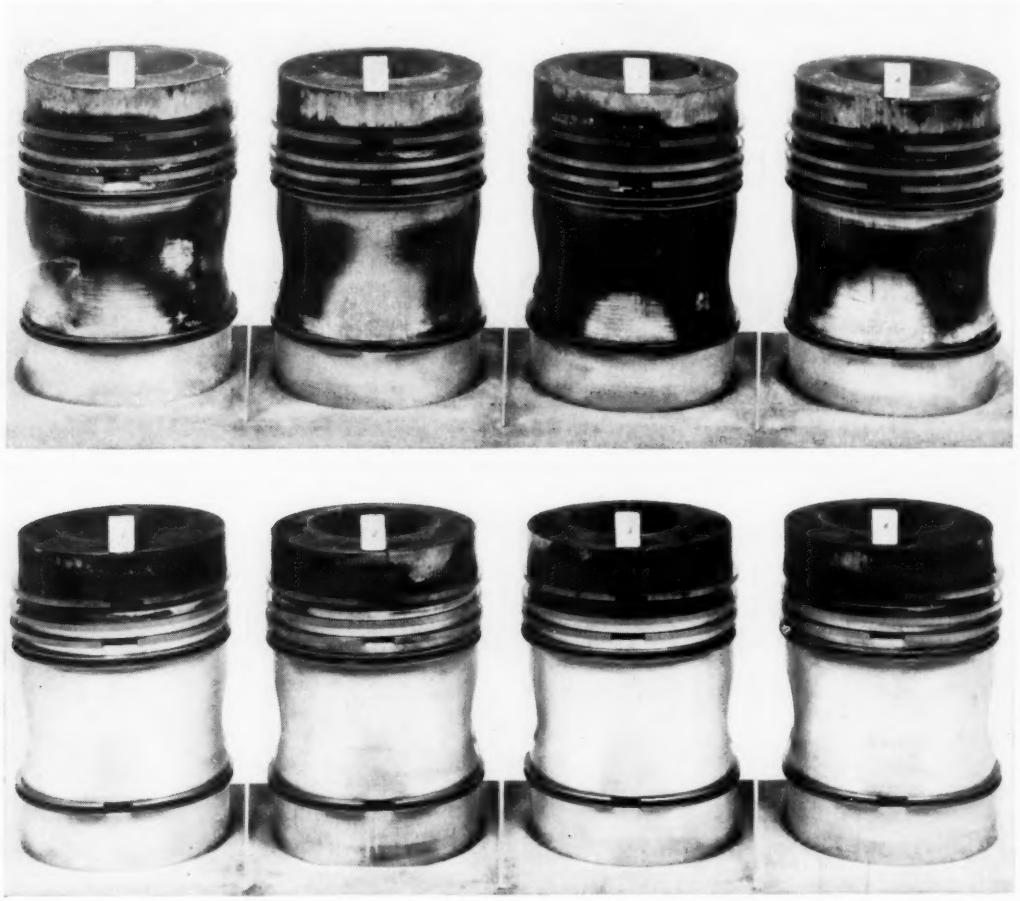

Figure 4—Comparison of pistons from Caterpillar D-4400 Test showing performance of poor oil (top) with a satisfactory heavy-duty detergent type oil (below)

ANTI-CORROSIVES

With the continuation of improvements in automotive, Diesel and aircraft engine design permitting the development of more power for the equivalent size and weight engine, new materials were necessary to withstand the higher stresses imposed. Chief among these was the improvement of bearings. The demand for greater load-carrying capacity and higher fatigue resistance fostered the development of bearing metals other than babbitt; i.e., copper-lead, lead plated silver, cadmium-silver, and cadmium-nickel alloys.

It was soon found, however, that the usual well-refined uninhibited oils could be very corrosive to these bearings, especially at the high temperatures obtained in automotive, aircraft, and high-speed Diesel engines. Corrosion of bearings is generally attributable to a reaction between the acidic products of oxidation and one of the constituents of the bearing metal. For example, the acids formed by the oxidation of the oil will attack the lead in copper-lead bearings taking it into solution and leaving a porous copper structure which will eventually crumble and break away.

Bearing corrosion may be controlled either by inhibiting oxidation completely so that no acidic bodies are formed (which is indeed a very difficult

thing to do) or by laying down a protective film on the surface of the bearing so as to prevent the acids from reaching the metal. Materials which function by forming such a protective coating are known as anti-corrosives or corrosion inhibitors. Compounds containing active sulfur, phosphorus, or nitrogen show the most promise in this respect. Materials containing sulfur seem to be especially effective due to their ease in forming protective films. These anti-corrosives may take the form of organic sulfides, phosphites, metal salts of thiophosphoric acids, and sulfurized waxes, to name a few.

Figure 5—Comparison of pistons from General Motors Diesel 500-hr. Test—note condition of piston on ordinary motor oil shown at left, compared with piston on heavy-duty detergent type oil shown at right.

Anti-Corrosives Also Act As Catalyst "Poisons"

It should be pointed out that anti-corrosives by virtue of their film-forming properties may also function as "poisons" for other metal surfaces in an engine. As a result, since the catalytic effects of the metal parts are decreased, the degree of oil oxidation is reduced materially. It is obvious, therefore, that when anti-corrosives are used in conjunction with anti-oxidants, bearing corrosion is reduced, while at the same time the life of the oil is extended more than if an anti-oxidant were used alone.

DETERGENTS

The dictionary defines the action of detergency as the cleansing or purging away of foul or offending matter. As mentioned previously, detergents were the first type of additives to be used in Diesel engines back in the '30's for the prevention of ring sticking and piston scuffing. The term detergent has since been used to classify additives which have the property of preventing the build-up of any deposits, or removing those already formed (be it sludge, varnish, lacquer, or carbonaceous products) which interfere with the efficient operation of internal combustion engines. These materials, which originate from oil deterioration as well as from combustion chamber blow-by, are a considerable problem, particularly in heavy duty equipment.

Various metallo-organic compounds such as phosphates, phenolates, alcoholates, naphthenates, and sulfonates have been found very useful for this purpose. At one time the belief existed that only certain soaps or salts of the alkaline earth metals (calcium, barium, magnesium, and strontium) were effective as detergents. Later developments, however, have revealed that high molecular weight soaps or organic salts of a number of other metals,

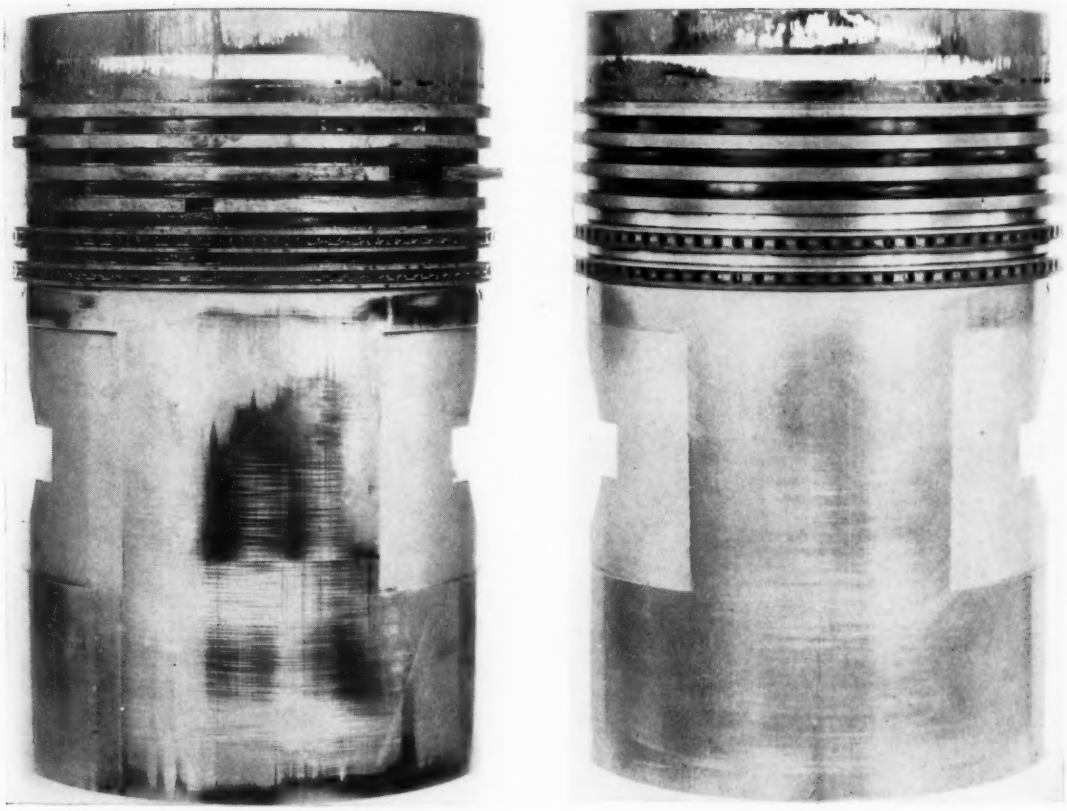

Figure 6—Showing the effectiveness of detergents in preventing piston deposit build-up in a Diesel engine. Test pistons from a super-charged Caterpillar test engine. At left is piston from an engine run on straight mineral oil; at right, piston from an engine run on the same oil containing a detergent type additive.

such as tin, and cobalt, also possess this desirable property.

The exact mechanism whereby a detergent functions is not too well understood but it may involve either one, or both, of the following preventive actions, in addition to the possible cleansing action usually attributed to it.

1. Detergents may act as oxidation directors so as to cause soluble oxidation products to form rather than oil insoluble ones.
2. A chemical reaction may take place between the detergent and the potential lacquer and sludge-forming molecules which prevents them from becoming insoluble materials to be deposited on various engine parts.

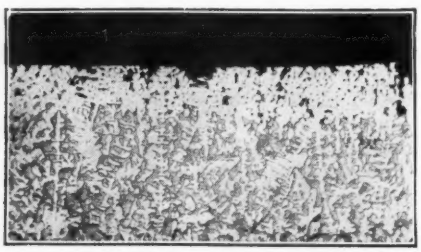

Figure 7—Photomicrograph (100X) of cross-section of a copper-lead bearing. Absence of lead (gray area) at surface indicates corrosion.

Since these additives may function so as to prevent rather than remove deposits, the term "detergent" is falling into disfavor in some circles. Nevertheless, regardless of their mechanism, it should be emphasized that detergents serve a very important function in promoting the engine cleanliness properties of lubricating oils especially for high-speed automotive and Diesel equipment.

Dispersants

The action of dispersion in a lubricating oil is of a physical nature in that the products of fuel combustion, chiefly soot, along with some oil decomposition products are held in suspension in the oil. This appears to be accomplished by the breakdown of these contamination particles into a finely divided state, or maintaining them in their original colloidal state. By this action, agglomeration of the particles is prevented with the result that oil filters

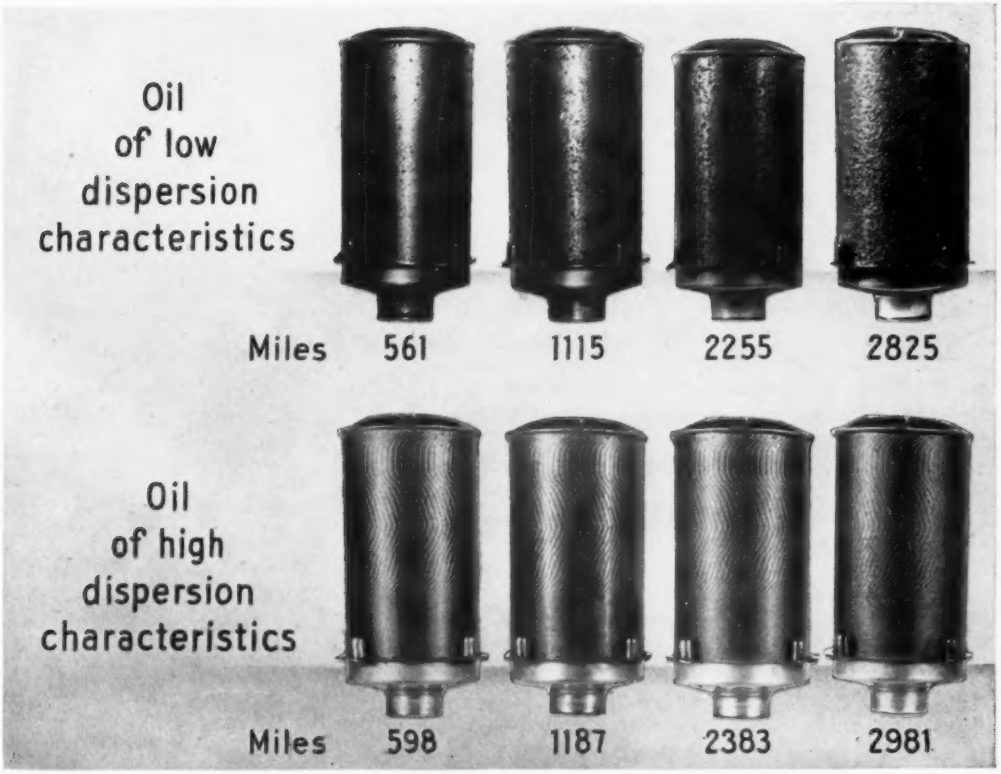

Figure 8—Dispersion effect of lubricating oil on oil strainers—top line of strainer elements shows effect of oil of low dispersion characteristics. Bottom line shows effect of oil of high dispersion characteristics.

and strainers remain unclogged for longer periods of time, and are thus better able to perform their function of removing from the oil stream any materials (such as dust) which might act as abrasives in the engine.

The ability of oils containing dispersants to retain carbon black (which may be considered comparable to blow-by soot) in suspension is shown in Figure 9. It will be observed that the carbon black has settled to the bottom in one instance denoting low dispersion, while it remains suspended in the oil in the other case indicating good dispersion properties.

The property of dispersion cannot be pinned down as being characteristic of any particular type of chemical compound. Although the phenomenon of detergency employs dispersion to a large extent, the two properties should be considered separately. This is readily appreciated when one considers that while all detergents seem to have good dispersion properties, not all oils with high dispersion values display satisfactory detergency.

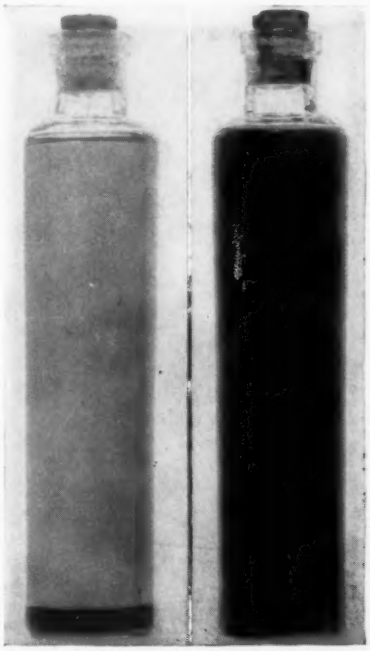

Figure 9—Comparison of oils of low and high dispersion by laboratory dispersion test. Bottle on left shows oil of low dispersion, while bottle on right shows oil of high dispersion.

EXTREME PRESSURE AGENTS

It is of paramount importance that a lubricant maintain a film between moving metal surfaces. Under operating conditions where the clearances are

relatively large, the problem is simply one of selecting the proper viscosity grade of oil. In service where pressures are high, however, as in hypoid gear lubrication, the lubricant is forced out and seizure of the metals may occur. As a result, additives known as extreme pressure (E.P.) agents were developed to impart the necessary high load-carrying properties to the lubricant.

A number of different types of compounds have been found to increase the load-carrying properties of lubricants. Certain phosphorus compounds such as tricresyl phosphate are very effective in reducing welding. Sulfur compounds of the sulfurized lard oil type are even more effective as are chlorinated materials also. In addition to compounds containing phosphorus, sulfur, and chlorine, moreover, lead soaps, such as lead naphthenate, are used to impart E.P. properties to lubricants.*

POUR POINT DEPRESSANTS

The pour point of an oil is the lowest temperature at which the oil flows under conditions established by the A.S.T.M. procedure. Some lubricating oils contain wax, the presence of which raises the pour point of the oil. Although the problem of pour has always been more or less in the minds of oil refiners and equipment users, the need for oils which would flow freely at extremely low temperatures was emphasized during World War II by the Army Ordnance inasmuch as some army equipment had to be used in very cold climates. Wax is removable by various methods, but in order to avoid the excessive costs involved where drastic dewaxing operations are needed, and at the same time to retain this high viscosity index material, pour depressants have been developed which reduce the pour point of wax-containing lubricants.

Examples are given below to indicate how such additives, which are usually very high molecular weight condensation products, effectively reduce the pour point of an oil.

Composition	*Pour Point, °F.*
SAE 30 Motor Oil "X"	+30
SAE 30 Motor Oil "X" plus 1.0% Pour Depressant "A"	—10
SAE 30 Motor Oil "Y"	+20
SAE 30 Motor Oil "Y" plus 0.16% Pour Depressant "B"	—15

Although a number of theories have been advanced to explain how pour depressants function, the most widely accepted one is that these materials coat the surface of the minute wax crystals. In this way both crystal growth and oil absorption by the wax are prevented at reduced temperatures. As a result, no gel formation occurs and the oil is free to flow at low temperatures.

*LUBRICATION, August, 1944.

VISCOSITY INDEX IMPROVERS

The physicist defines viscosity as a measure of the relative fluidity of a liquid at some specific temperature.* Viscosity will vary inversely with temperature, i.e., the colder the oil, the heavier or more sluggish will it become. As the temperature is raised, the same oil will become more and more fluid. Viscosity index indicates the rate of change of the viscosity of a lubricating oil with temperature. The higher the viscosity index, the less the viscosity of the oil changes with temperature.

Viscosity index (V.I.) by itself is not indicative of the oxidation stability or performance qualities of a lubricating oil. Low V.I. oils may give as good performance as high V.I. oils. In machinery where starting temperatures are unimportant, such as stationary engines operated inside buildings, low viscosity index oils have been used quite extensively for years with excellent results.

In order to be able to extend the usable temperature range for low V.I. oils for automotive engine service, and for hydraulic oil systems, however, where starting and operating temperatures are sometimes quite low, it has been found necessary to develop viscosity index improvers. These materials usually consist of high molecular weight compounds or highly polymerized materials such as products of unsaturated hydrocarbons, fatty acids, etc. The effect of such materials is illustrated below.

V.I. Improver % Added	*Saybolt Universal Viscosity @ 210° F.*	*Viscosity Index*
0.0	49.2	26
0.5	54.0	51
1.5	66.0	86

The above data shows that by use of a V.I. improver the viscosity at elevated temperatures within the operating range can be raised to assure more body in the oil film; yet the same oil at temperatures over the cold starting range will be sufficiently fluid to assure easy starting and distribution throughout the oiling system.

SUMMARY

A rather brief presentation has been made of some of the most important types of lubricating oil additives. Great strides have been made in recent years in the development of superior additives, particularly of the anti-oxidant, anti-corrosion, and detergent types, for improving the properties of lubricating oils. The story of additives is by no means closed, however. New and interesting chapters are continually opening up and older chapters are being revised. The almost miraculous potentialities of these addition agents present a constant and inspiring challenge to the oil technologist.

*LUBRICATION, April, 1945.

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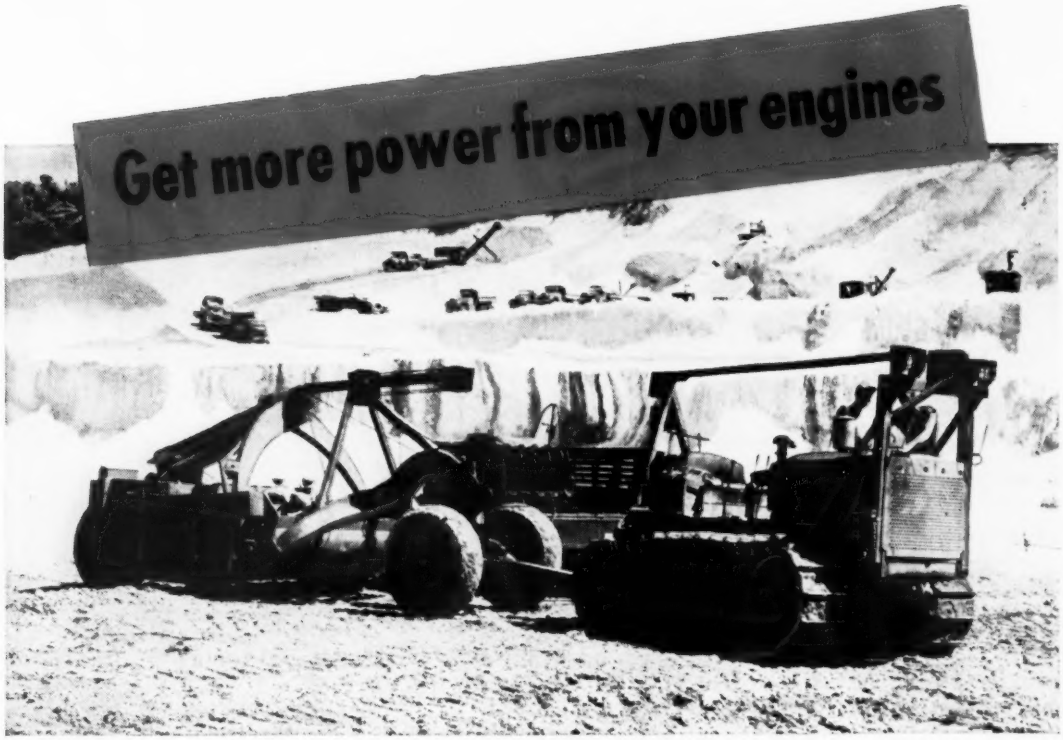

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